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Interpreting elevated space-borne HCHO columns over the Mediterranean Sea using the OMI sensor

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Abstract. Formaldehyde (HCHO) is an oxidation product of a wide range of volatile organic compounds (VOCs) and important atmospheric constituent found in both the polluted urban atmosphere and remote background sites. In this study, remotely sensed data of HCHO vertical column densities are analyzed over the Mediterranean Sea using the Ozone Monitoring Instrument (OMI). Data analysis indicates a marked seasonal cycle with a summer maximum and winter minimum confined to the marine environment during a three year period (2005–2007) examined. A possible retrieval artifact associated with Saharan dust transport over the region is explored by changing intensity of Saharan dust sources in GEOS-Chem following the recommendation of Generoso et al. (2008). Recalculated air mass factors (AMF), based on the new values of aerosol loadings, lead to a reduction of the summertime “hot spot” in OMI retrieval of HCHO vertical columns over the Mediterranean Sea; however, even after the correction, enhanced values are still present in this region. To explain these values, marine biogenic sources of VOCs are examined. Calculations indicate that emission of phytoplankton-produced isoprene is not likely to explain the enhanced HCHO vertical columns over the Mediterranean Sea. Model simulations in conjunction with measurements studies may be required to fully explore the complex mechanism of HCHO formation over the Mediterranean and its implications for the air quality in the region.

1 Introduction

Formaldehyde (HCHO) is one of the most abundant carbonyl compounds in both the polluted urban atmosphere and remote background sites (Ayers et al., 1997; Lee et al., 2001;

Singh et al., 2001; Grosjean et al., 2002). Formaldehyde can be directly emitted from anthropogenic (automobile exhaust, industrial emissions, biomass burning) (Carlier et al., 1986; Sigsby et al., 1987; Andreae and Merlet, 2001) and natural sources (vegetation) (Kesselmeier and Staudt, 1999; Seco et al., 2007) or photochemically produced through the oxidation of volatile organic compounds (VOCs) (Finlayson-Pitts and Pitts, 1997; Crutzen et al., 1999). The lifetime of HCHO in the atmosphere is controlled by two main sinks: photolysis and reaction with hydroxyl radical (OH). At low OH concentrations (5×10^5 molecules cm^{-3}) and high OH concentrations (1×10^7 molecules cm^{-3}), the lifetime of HCHO can be 60 h to 3 h, respectively (Dufour et al., 2009). Although the photo-oxidation of methane (CH_4) is the main source of HCHO in the background atmosphere, the additional oxidation of non-methane VOCs (e.g., isoprene and monoterpenes) can significantly contribute to local HCHO concentrations (Fehsenfeld et al., 1992; Fuentes et al., 2000). Short lived VOCs with high HCHO yields (e.g., isoprene) can cause localized “hot spots” over certain regions (e.g., Southeastern United States) while the HCHO enhancement from the oxidation of longer lived VOCs will be spread over larger areas, causing a more uniform distribution. Based on this postulation, several studies have successfully used remotely sensed formaldehyde as a “top-down” approach to constrain terrestrial isoprene concentrations (Abbot et al., 2003; Palmer et al., 2003, 2006; Shim et al., 2005; Millet et al., 2008; Barkley et al., 2008; Stavrou et al., 2009; Dufour et al., 2009; Curci et al., 2010).

Past studies focusing on VOC emissions from Europe revealed remarkably high summertime HCHO mixing ratios over the Mediterranean Sea, that was not well simulated by chemical transport models (Lelieveld et al., 2002; Kormann et al., 2003; Ladstätter-Weissenmayer et al., 2003, 2007; Curci et al., 2010; Klippel et al., 2011). Since HCHO has a high solubility in water, with a Henry Law constant of $\sim 6 \times 10^3$ mol atm^{-1} (Sander, 1999), it is generally assumed



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that there are no direct emissions from the ocean (Mopper and Stahovec, 1986). Therefore, formation of formaldehyde with marine sources is most likely from the photo-oxidation of phytoplankton-produced VOCs. Previous studies have shown that considerable amounts of isoprene and, to much lesser extent, monoterpenes can be produced by marine phytoplankton (Bonsang et al., 1992; Moore et al., 1994; Shaw et al., 2003, 2010; Broadgate et al., 2004; Yassaa et al., 2008). It was proposed that incoming solar radiation and water temperature can significantly affect marine isoprene (Shaw et al., 2003; Gantt et al., 2009) and monoterpene (i.e., α - and β -pinene, Sabolis, 2010) emission rates, making dynamic marine areas (such as upwelling regions and estuaries) likely regions for higher marine biogenic VOC emissions compared to the global average. Although oxidation of marine VOCs can lead to the formation of HCHO, it is not clear if the rates of phytoplankton-produced VOCs are high enough to enhance HCHO signals above the background levels (determined by CH₄ oxidation) and create the hot spots over marine environments large enough to be identified using remotely sensed techniques.

In this study, remotely sensed formaldehyde vertical column densities from the Ozone Monitoring Instrument (OMI) satellite sensor (Levelt et al., 2006) for the years 2005–2007 are used to explore this potential marine source of VOCs in the region of the Mediterranean Sea. Previous work illustrated that such an approach can be effective when the parent VOC has a significant HCHO yield and sufficiently short lifetime to have local relationship between the emissions of the VOC and the retrieved HCHO vertical columns (Palmer et al., 2003, 2006). Currently the origin for enhanced summertime concentrations of HCHO over the Mediterranean Sea is not clear and is suggested to be related to one or more processes such as summertime transport of continental air masses, transport of Saharan dust, intense ship traffic, and changes in surface temperature and nutrient stratification, influencing marine biota (Curci et al., 2010). This study addresses the following two questions: Does OMI consistently reveal enhanced HCHO vertical columns over the Mediterranean Sea? If so, is the cause due to satellite retrieval error and/or ocean biological source (i.e., oxidation of marine isoprene)?

2 Data and methods

2.1 HCHO remote sensing

Data from the OMI sensors was used in this study for the retrieval of HCHO vertical columns over the Mediterranean region. OMI is aboard NASA's EOS-Aura satellite (<http://aura.gsfc.nasa.gov/>) with a sun-synchronous polar orbit and an equator crossing time of 13:38 local time. OMI has a 2600 km viewing swath, with pixel sizes ranging from 13 × 24 km at nadir to 26 × 135 km at the swath edges, allowing

for almost daily global coverage (Millet et al., 2008). OMI is a nadir viewing UV/Vis sensor observing continuously from 270 to 500 nm (Kurosu et al., 2004).

Retrieval of HCHO vertical columns starts with the retrieval of slant column density (SCD), which essentially is the HCHO concentration integrated along the viewing path of the satellite. The retrieval algorithm for OMI HCHO SCD is based on a non-linear least-squares fitting. OMI SCDs are determined by fitting measured radiances using a spectral window between 327.5–356.5 nm (OMI-ATBD, 2002) using the GOME algorithm (Chance et al., 2000), including the Chance et al. (2005) sampling correction. Vertical columns are then calculated by dividing slant columns over a calculated Air Mass Factor (AMF). The AMF takes into account atmospheric scattering, surface albedo, satellite viewing geometry, aerosols, clouds, and the vertical distribution of HCHO. The calculation of the AMF used for conversion of a SCD into a vertical column has two parts: the use of a chemistry transport model (CTM) to generate the “shape factor” (the normalized vertical profile of HCHO concentration) and a radiative transfer model within the CTM to generate “scattering weights” (the vertical profile of the sensitivity of backscattered spectrum to HCHO abundance) (see Palmer et al., 2001 and Martin et al., 2002 for details). OMI data products use the GEOS-Chem global 3-D chemical transport model (Bey et al., 2001; Palmer et al., 2001; Martin et al., 2002; see Figs. S1–S2 for sample HCHO profiles and distribution) and the LIDORT radiative transfer model (Spurr et al., 2001) for the calculation of the AMF.

For OMI retrievals we use Level 2 (v003) geolocated data products (<http://mirador.gsfc.nasa.gov/>). Clouds in the satellite viewing scenes have been identified as the primary source of error in the retrievals (Millet et al., 2006); therefore, satellite data are gridded at a $0.25^\circ \times 0.25^\circ$ resolution with data pixels of cloud fractions <20 %. The uncertainty on a single HCHO slant column is $\sim 8 \times 10^{15}$ molecules cm⁻² and in relative units it ranges 40–100 % (Chance and Kurosu, 2008; Curci et al., 2010), while the uncertainty on the AMF calculated with GEOS-Chem is estimated to be about 30 % for cloud fractions less than 0.2 (Millet et al., 2006; Palmer et al., 2006). The total uncertainty of a single HCHO vertical column ranges from 50 to 105 % (Chance and Kurosu, 2008; Curci et al., 2010). When considering regionally and temporally averaged vertical columns, the random error on the slant columns of the OMI sensor is reduced by the square root of the number of observations (~ 10 –30 for monthly averages) included in the mean.

We use GEOS-Chem version 7.03 with GEOS-4 assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office regridded to a horizontal grid resolution of $2^\circ \times 2.5^\circ$ (latitude-longitude) and 47 vertical layers. In its full chemistry configuration, GEOS-Chem includes H₂SO₄-HNO₃-NH₃ aerosol thermodynamics coupled to an O₃-NO_x-hydrocarbon-aerosol chemical mechanism (Bey et al., 2001;

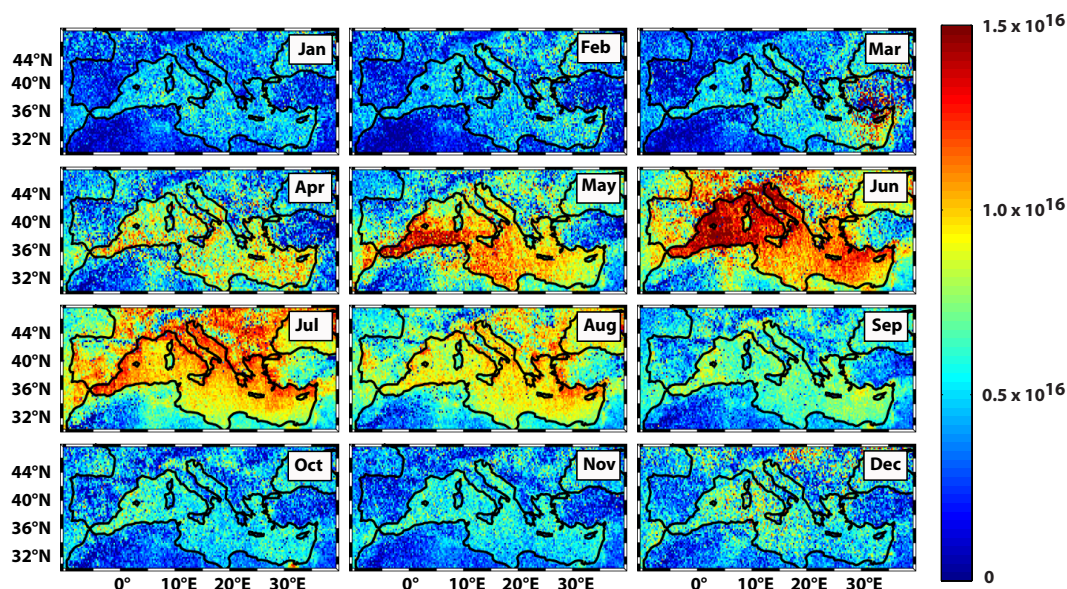


Fig. 1. Monthly averaged (from 2005 to 2007) OMI retrieved formaldehyde vertical columns in units of molecules cm^{-2} .

Park et al., 2004). Sulfur compounds, carbonaceous aerosols, and sea-salt emission and chemistry are accounted for and described by Park et al. (2004), Heald et al. (2005), and Alexander et al. (2005).

2.2 Biogenic sources

It has been well documented (both in laboratory and field studies) that phytoplankton can emit several types of biogenic VOCs, including isoprene (Bonsang et al., 1992; Shaw et al., 2003, 2010; Gantt et al., 2009). Owing to its short lifetime and relatively high HCHO yield (Palmer et al., 2003, 2006), isoprene can potentially contribute to local HCHO vertical columns. It is a common practice to characterize marine emissions of isoprene by using remotely sensed surface chlorophyll-*a* concentration ([Chl-*a*]) as a proxy for the phytoplankton abundance in the surface layer. However, satellite based retrievals of [Chl-*a*] are not sufficient to describe the phytoplankton abundance in the Mediterranean Sea. Due to strong vertical mixing, nutrients accumulate at the surface throughout the winter months. With the springtime increase in sea-water surface temperatures and incoming solar radiation, these stored nutrients can fuel biological productivity in the upper water column (Marty et al., 2002). By the summertime, the nutrients get depleted and strongly-stratified oligotrophic (lacking essential nutrients to support primary productivity) surface waters can no longer sustain plankton growth. Under such conditions, phytoplankton in the Western and Eastern parts of Mediterranean Sea move lower in the water column at ~ 50 m and ~ 100 m, respectively (Crise et al., 1999) to the depth that is usually not sampled by the satellites. Due to the seasonal formation of this deep chlorophyll maximum, satellite retrieval of [Chl-*a*]

may not be an accurate representation of the full water column biomass. Because of such difficulties in remotely sensed [Chl-*a*] retrievals in the Mediterranean Sea, to get an accurate representation of the biomass of marine organisms within the water column we use two satellite-based calculations of the column integrated net primary production (NPP, $\text{mg C m}^{-2} \text{ day}^{-1}$) as a proxy for a marine VOC source. One NPP calculation is the Vertically Generalized Production Model (VGPM) (Behrenfeld and Falkowski, 1997) which incorporates satellite-derived [Chl-*a*], sea surface temperature, cloud-corrected incident daily photosynthetically active radiation (PAR), and the day length. The other NPP calculation is the Carbon-based Productivity Model (CbPM) (Behrenfeld et al., 2005; Westberry et al., 2008) which is a function of [Chl-*a*], particulate backscattering coefficients, PAR, diffusion attenuation at 490 nm wavelength, mixed layer depth, nitrocline depth, and the day length. In comparison to satellite-derived [Chl-*a*], these NPP calculations are believed to be a more accurate proxy for phytoplankton biomass in oligotrophic regions. The 8-day averaged NPP products are obtained from <http://www.science.oregonstate.edu/ocean.productivity/custom.php> based on input from Moderate Resolution Imaging Spectroradiometer (MODIS)-Aqua and regridded from $\frac{1}{12}^\circ \times \frac{1}{12}^\circ$ to $0.25^\circ \times 0.25^\circ$ resolution.

3 Results

3.1 OMI AMF correction

Analysis of remotely sensed data reveals that the HCHO hot spot typically appears over the Mediterranean during the warmer seasons. Figure 1 shows that during winter months,

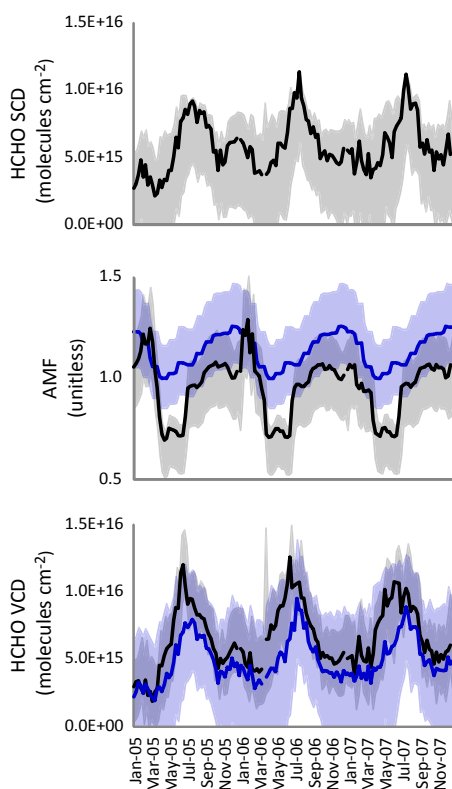


Fig. 2. Time series of 8-day averaged OMI HCHO (a) slant column density, (b) air mass factor, and (c) vertical column density from January 2005 to December 2007 for the standard (black) and corrected (blue) datasets. The data was averaged over entire Mediterranean Sea. Shaded area represents one standard error about mean observation.

the magnitude of HCHO vertical columns is low in all areas over the Mediterranean region ($\sim 3 \times 10^{15}$ molecules cm^{-2}). However, in late spring to summer months vertical columns are greatly enhanced over the western Mediterranean Sea. Figure 1 also shows some spatial variations: the western part of the Mediterranean displays higher summertime HCHO vertical columns compared to the eastern region. One of the possible reasons for such enhanced summertime HCHO vertical columns could be the presence of mineral dust in a viewing path of the satellite. Due to its proximity to the Sahara Desert, there are frequent intrusions of large dust in the Mediterranean Sea area. Although dust events are largely variable, climatological records indicate a seasonal cycle coinciding with the dry season; specifically, a maximum occurs during spring in the Eastern Mediterranean and during summer in the Western Mediterranean (Moulin et al., 1998). Moreover, persistent dust haze conditions (typically lasting 1–3 days) impact the Western Mediterranean more frequently than the eastern part (Pye, 1992). Therefore, to understand enhanced HCHO vertical columns over the Mediterranean Sea, we first examine the possible retrieval artifacts associated with Saharan dust transport over the region.

Figure 2a shows time series of 8-day averaged OMI AMF generated using GEOS-Chem and the LIDORT radiative transfer model. In this figure there is a pronounced reduction of AMFs from March to June for all three years examined. The AMF values depend on atmospheric scattering and the vertical distribution of the species. Therefore the presence of aerosols above trace gases such as HCHO in the vertical atmospheric column should lead to a strong decrease of the AMF. When satellite retrieved HCHO SCDs are divided by the reduced AMF values, higher values for vertical columns are attained (see Fig. 2b, c). However, it has recently been reported that GEOS-Chem may overestimate dust abundance for Saharan dust sources (Generoso et al., 2008). Such overestimation of Saharan dust, plumes of which often extend up to 8 km (Generoso et al., 2008), could cause excessive reduction in AMF values and increases in HCHO vertical columns. Here we have followed recommendation of Generoso et al. (2008) and reduced Saharan dust emissions by a factor of three. Figure 2c shows that these corrected AMF values yield considerably lower OMI HCHO vertical columns for the all three years. Figure 3 shows that corrected AMFs lead to significant reduction of the OMI retrieved HCHO vertical columns for both the western and the eastern parts of the Mediterranean Sea. Comparison of Figs. 1 and 3 shows that when the new AMF values are employed, HCHO column densities are lowered by $\sim 40\%$ in June and by $\sim 10\%$ in July and August. The recalculated AMFs also removed fictitious early-summertime west-east gradient associated with the excessive model dust over the Western Mediterranean. However, it should be noticed, that despite the reduction in the original HCHO hot spot, there is still an enhancement in the HCHO vertical columns confined over the water.

3.2 Possible marine biogenic sources of HCHO over the Mediterranean Sea

The Mediterranean is naturally oligotrophic (i.e., low nutrients and therefore low productivity), with an increase to ultraoligotrophic waters in the eastern section (Pedrós-Alió et al., 1999; Turley, 1999). However, during the winter, surface waters cool leading to a breakdown in the thermohaline circulation. This breakdown allows for vertical mixing between the deep-nutrient rich waters and the oligotrophic surface waters (Turley, 1999; Pedrós-Alió et al., 1999; Turley et al., 2000), especially in the Northwestern Mediterranean. Nutrients upwelled in winter facilitate primary production in the surface waters reaching highest levels in April, before decreasing again in summer. Figure 4 shows that the western Mediterranean has a considerable amount of productivity in the spring and summer ($> 500 \text{ mg C m}^{-2} \text{ day}^{-1}$ with isolated areas over $1000 \text{ mg C m}^{-2} \text{ day}^{-1}$) while the eastern Mediterranean is less productive ($< 300 \text{ mg C m}^{-2} \text{ day}^{-1}$). The enhancements of marine biological productivity in the Mediterranean and Atlantic Ocean (i.e., the Bay of Biscay,

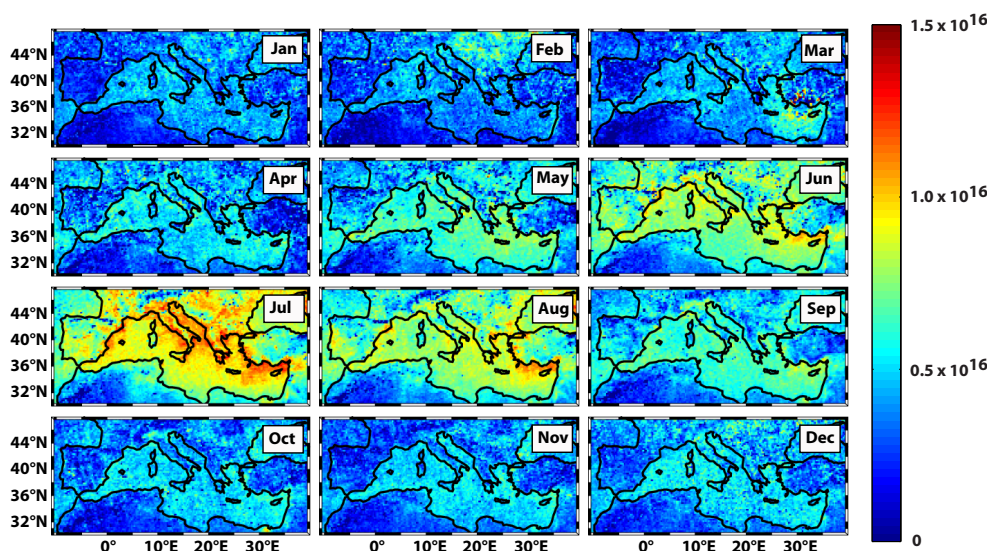


Fig. 3. Monthly averaged (from 2005 to 2007) retrieved formaldehyde vertical columns in units of molecules cm^{-2} . The vertical columns are recalculated using corrected AMF values. See text for more details.

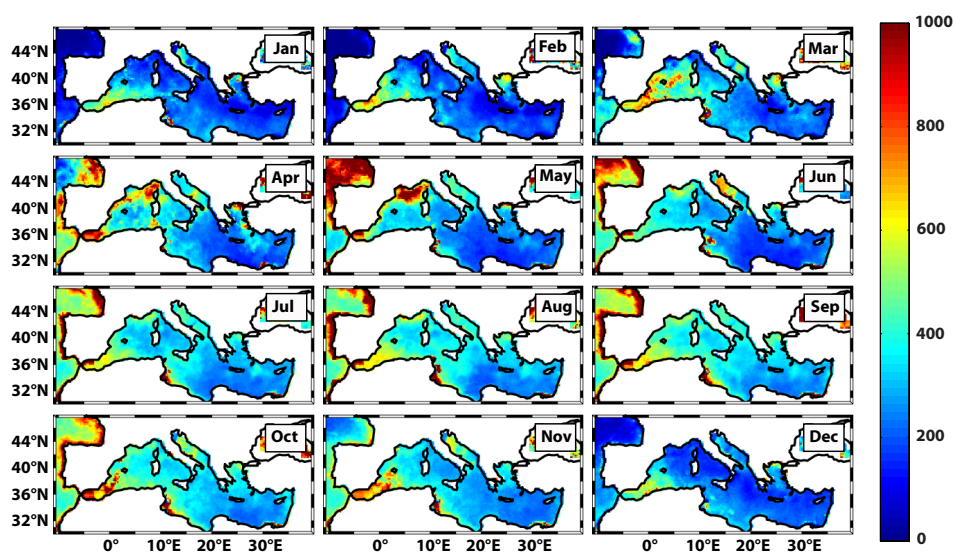


Fig. 4. Monthly averaged (from 2005 to 2007) net primary production (NPP) in units of $\text{mg C m}^{-2} \text{ day}^{-1}$ from the Carbon-based Production Model (CbPM) based on input from MODIS-Aqua.

off the coast of Portugal, the coast of Italy and at the mouth of the Nile River Delta) in May are diminished by August (see Fig. 4), leading to an ultraoligotrophic environment. Comparison of Figs. 3 and 4 show that there is little similarity (either spatially or temporally) between the NPP in the Mediterranean Sea and the atmospheric column concentrations of HCHO. In general, the areas with the highest HCHO vertical columns (both within the Mediterranean region and outside) do not coincide with the areas with the highest NPP. The temporal variation of the NPP and HCHO vertical columns for the Bricaud et al. (2002) sub-regions of the Mediterranean

(Fig. 5) also show little relationship between HCHO and NPP for all regions with the NPP typically peaking in the spring and HCHO vertical columns in the summer. In several sub-regions in the southern Mediterranean, there is little seasonal variation in the NPP while the HCHO vertical columns have a well-defined seasonal cycle. Scatterplots of the NPP and HCHO vertical columns for each $0.25 \times 0.25^\circ$ grid (Fig. 6) show little relationship between the two variables regardless of NPP calculation method and anthropogenic/terrestrial aerosol influence (using aerosol optical depth as a proxy).

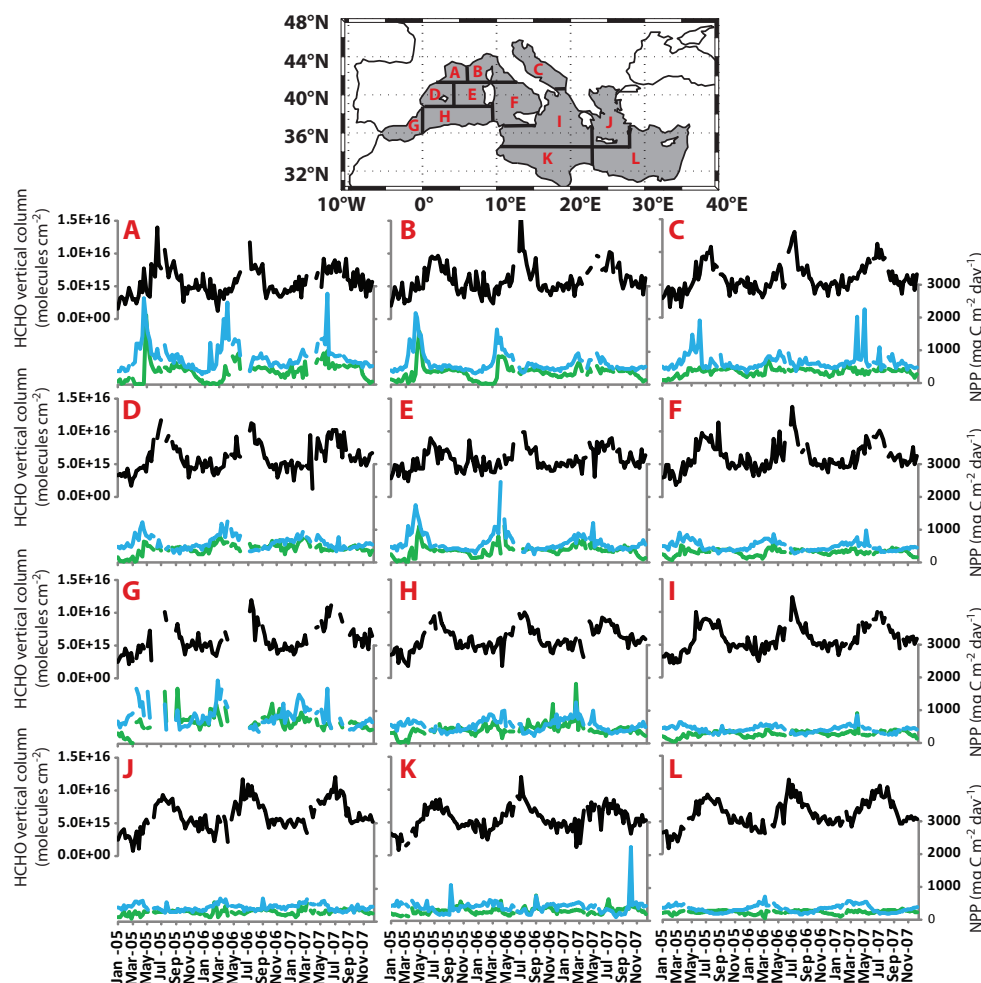


Fig. 5. Time series of 8-day averaged HCHO vertical columns from OMI (black) recalculated using corrected AMF values for January 2005 to December 2007 and the net primary productivity as estimated from the CbPM (green) and Vertically Generalized Production Model (VGPM) (blue) methods based on input from MODIS-Aqua and filtered to include only temporally and spatially collated $0.25 \times 0.25^\circ$ grids with 8-day averaged aerosol optical depth (AOD) < 0.2 (interpolated from $1 \times 1^\circ$ level 3 data at 550 nm from the MODIS-Aqua satellite). The Bricaud et al. (2002) Mediterranean Sea subregions are the (A) Gulf of Lions, (B) Ligurian Sea, (C) Adriatic Sea, (D) Balearic Sea, (E) Algero-provençal Basin, (F) Tyrrhenian Sea, (G) Alboran Sea, (H) Algerian Basin, (I) North Ionian Sea, (J) Aegean Sea, (K) South Ionian Sea, and (L) Levantine Basin.

Despite the absence of clear relationship between NPP and HCHO vertical columns, we use the method similar to Palmer et al. (2003) and estimate the amount of ocean-derived isoprene required to explain the retrieved column concentrations of formaldehyde over the Mediterranean Sea. According to Palmer et al. (2006) HCHO yields from oxidation of pinenes are only about one third those of isoprene and have minor contribution to HCHO vertical columns. Assuming a background HCHO concentration is due to methane oxidation and longer-lived VOCs, the HCHO vertical columns (Ω_{HCHO}) can be calculated as $\Omega_{\text{HCHO}} = S \times E_{\text{iso}} + B$, where S is the linear slope corresponding to HCHO yield from isoprene ($1.9 \times 10^3 \text{ s}$), E_{iso} is the isoprene emission rate, and B is the background HCHO

concentration (Palmer et al., 2003). The remotely sensed Ω_{HCHO} can be used to back-calculate the isoprene emission necessary for the observed HCHO. Palmer et al. (2003) showed that the assumption is valid in summer at midlatitudes for a high HCHO-yield and reactive (lifetime 30 min) parent VOC (i.e., isoprene). For the background HCHO concentration we use the lowest OMI-retrieved value ($\sim 3 \times 10^{15} \text{ molecules cm}^{-2}$) over the Mediterranean basin during the month of January. By solving the equation for E_{iso} we estimate that the lowest isoprene emission required to explain the summertime maxima in the retrieved OMI HCHO vertical columns ($\sim 1.2 \times 10^{16} \text{ molecules cm}^{-2}$ as shown in Fig. 3 for July) is $\sim 5 \times 10^{12} \text{ atoms C cm}^{-2} \text{ s}^{-1}$. This isoprene emissions rate is ~ 2 to 3 orders of magnitude higher than recent

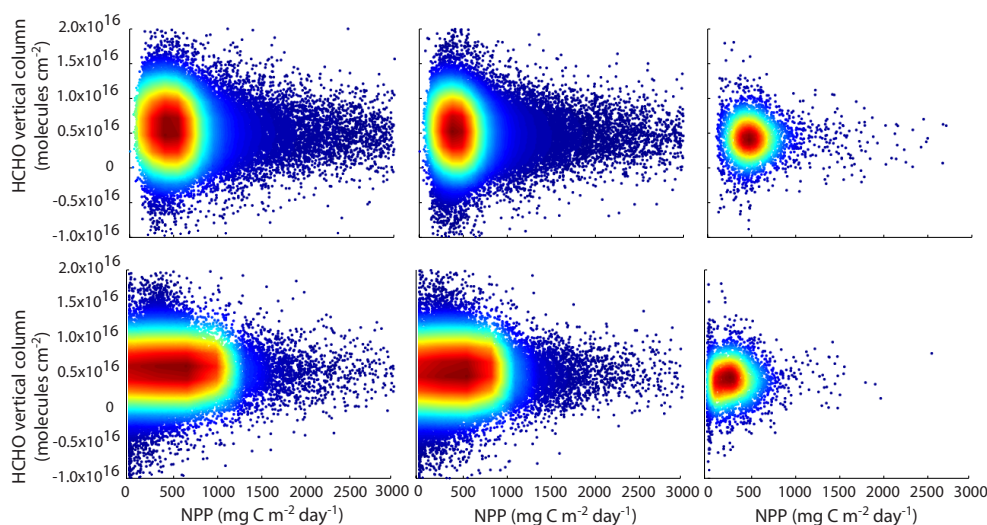


Fig. 6. Scatterplot of VGPM (top row) and CbPM (bottom row) NPP based on input from MODIS-Aqua and OMI HCHO vertical columns recalculated using updated AMF from the Mediterranean Sea subregions for $0.25 \times 0.25^\circ$ grids with no MODIS-Aqua AOD filter (right column), AOD < 0.2 (center column) and AOD < 0.05.

estimates of marine isoprene emissions in the Mediterranean Sea (Liakakou et al., 2007) and outside the range of uncertainty due to variability in [Chl-*a*] and laboratory measured isoprene emission rates (Shaw et al., 2003, 2010; Palmer and Shaw, 2005; Gantt et al., 2009; Sabolis, 2010). Although this simplified approach is in no way revealing the actual marine isoprene emissions over the Mediterranean, it does provide a rough estimate of the contribution needed in order for primary productivity to be the major source of the remotely sensed HCHO vertical columns over the Mediterranean Sea. Therefore, based on the comparison of laboratory measured isoprene emission rates and the ones estimated using remotely sensed data, we conclude that marine isoprene emissions associated with primary productivity in the Mediterranean Sea is not likely to be an important source of the retrieved summertime vertical columns of HCHO.

3.3 Comparison with previous results

The summertime Mediterranean basin is directly under the descending branch of the Hadley circulation, driven by deep convection in the Inter-Tropical Convergence Zone (Lelieveld et al., 2002). Owing to cloud-free conditions and higher solar radiation intensity, VOCs in the air masses transported from the surrounding regions (e.g., Central Europe, Balkans) and distant areas (e.g., Asia and North America) are subject to intense photochemical degradation. The large-scale subsidence also limits upward dispersion of pollutants (Ladstätter-Weissenmayer et al., 2003), causing strongest anthropogenic influence to be detected in the lower 4 km over the Mediterranean basin (Lelieveld et al., 2002). Previous in situ measurements and remotely sensed data revealed remarkably high HCHO mixing ratios over the Mediterranean

(Lelieveld et al., 2002; Kormann et al., 2003; Ladstätter-Weissenmayer et al., 2003, 2007; Klippel et al., 2011). In general, reported HCHO concentrations were highest in the marine boundary layer (up to 1500 ppt) and decreased with increasing altitude (Kormann et al., 2003). GOME (Global Ozone Monitoring Experiment) satellite retrieved HCHO vertical columns averaged over July and August, 2001 was 6.4×10^{15} molecules cm^{-2} , with occasional enhanced values of 1.1×10^{16} molecules cm^{-2} in the Eastern Mediterranean (Ladstätter-Weissenmayer et al., 2003). Over Crete (South East Mediterranean), monthly averaged HCHO vertical columns from GOME for 1996–2002 also showed highly enhanced monthly mean summertime values between 4×10^{15} and 8×10^{15} molecules cm^{-2} (Ladstätter-Weissenmayer et al., 2007). Although previously reported data cannot be directly compared to the results of the current study, it shows general consistency for highly elevated summertime concentrations of HCHO over the Mediterranean basin.

The exact reasons for such enhanced HCHO concentrations over the Mediterranean summer conditions (factor of 4 to 5 higher compared to Pacific background troposphere, Lelieveld et al. 2002) are not well understood. The model simulations consistently underestimate HCHO mixing ratios over the Mediterranean Sea (Ladstätter-Weissenmayer et al., 2003; Klippel et al., 2011). The discrepancy between model-predicted and measured HCHO concentrations over the Mediterranean region was suggested to be associated with the missing terpene chemistry (Ladstätter-Weissenmayer et al., 2003) and/or incomplete characterization of air mass trajectories (Kormann et al., 2003; Ladstätter-Weissenmayer et al., 2007; Scheeren et al., 2003). However, recent airborne campaign covering an area from the Mediterranean region in the south up to the subpolar regions north of

Norway revealed homogeneous distribution of formaldehyde everywhere, except over the Mediterranean, where strongly elevated summertime levels of HCHO were reported (Klippel et al., 2011). In fact, large discrepancies between model-predicted and measured HCHO concentrations over the marine boundary layer have been previously identified (Jacob et al., 1996). Although some measurement campaigns reported very low (50–250 pptv) HCHO mixing ratios over marine boundary layer, often without clear diurnal variation (Lowe and Schmidt, 1983; Mackay et al., 1996; Heikes et al., 1996), others report mixing ratios between 300 to 1000 ppt with a distinct diurnal cycle (Zafirov et al., 1980; Arlander et al., 1990, 1995; Ayers et al., 1997; Zhou et al., 1996; Weller et al., 2000; Singh et al., 2001; Fried et al., 2002). Such high mixing ratios (factor of 2 to 4 above what is typically predicted by photochemical models considering methane (CH_4) as the only source; Logan et al., 1981), point to a possible missing HCHO source in marine boundary layer. Potential new mechanisms for the enhanced production of HCHO such as reaction of methylperoxy (CH_3O_2) with hydroperoxyl radical (HO_2) (Ayers et al., 1997; Weller et al., 2000; Elrod et al., 2001) were shown not to be sufficiently important to explain measurement-model discrepancies (Fried et al., 2003). Results of our study, based on the comparison of laboratory measured ocean-isoprene emission rates and the ones estimated using remotely sensed data, suggest that contribution of ocean-derived terpenes (Ayers et al., 1997) is also not likely to be a main source of HCHO in marine boundary layer. Nevertheless, it should be noted that today very large discrepancies (factors of 30 for isoprene and 2000 for α -pinene) exist for marine VOC emission rates estimates based on the ambient measurements and laboratory data (Luo and Yu, 2010).

4 Conclusion

In this study, we use the Ozone Monitoring Instrument (OMI) remotely sensed formaldehyde (HCHO) vertical columns for the years 2005–2007 to explore unexpectedly high concentrations of HCHO observed over different parts of the Mediterranean Sea. The summertime enhancement of HCHO vertical columns in OMI retrievals is considerably diminished when Saharan dust emissions in GEOS-Chem are reduced by a factor of three following the recommendation of Generoso et al. (2008). The new values of aerosol loadings and the corrected air mass factors (AMFs) lead to a reduction of the summertime “hot spot” in OMI retrievals of HCHO over the Mediterranean Sea; however, even after the correction enhanced HCHO vertical columns over the Mediterranean are still present. Future studies should examine OMI HCHO vertical columns when GEOS-Chem model is driven by the Goddard Earth Observing System Model, Version 5 (GEOS-5) assimilated meteorological fields.

In addition to AMF corrections due to the presence of mineral dust over the Mediterranean Sea, possible sources associated with local photochemical production of HCHO are also explored. Marine biological sources of VOCs such as phytoplankton production of isoprene and monoterpenes do not seem to be probable sources for the enhanced HCHO concentrations over the Mediterranean Sea. The back-calculations show that marine isoprene emissions rates required for explaining the observed HCHO vertical columns are several orders of magnitude larger than previously estimated in laboratory experiments. It is unlikely that oligotrophic waters of the Mediterranean are capable of supporting such high emission rates.

This study adds further support to aircraft based measurements for elevated levels of formaldehyde over the Mediterranean Sea. Retrievals characterizing HCHO vertical columns with a defined seasonal cycle of a winter minimum and summer maximum, and large discrepancies between model-predicted and measured HCHO concentrations over the marine boundary layer are pointing to a possible photochemical source of HCHO over water bodies. According to this study direct production of VOCs by marine phytoplankton did not seem to be high enough to support elevated sources of HCHO; therefore we suggest future studies should examine abiotic mechanisms for formaldehyde production. Sea-water samples subjected to a natural sunlight revealed that low-molecular weight carbonyl compounds (including formaldehyde) and a whole suit of nonmethane hydrocarbons can be produced photochemically from the degradation of refractory dissolved organic matter (DOM) (Zhou and Mopper, 1997; Riemer et al., 2000). Although the net flux of formaldehyde is expected to be from air to sea, DOM has repeatedly been identified in submicron marine aerosol (O'Dowd et al., 2004; Leck and Bigg, 2005; Facchini et al., 2008; Ovadnevaite et al., 2011) photochemical aging of which can become a potential source of formaldehyde over the marine regions. Recent modeling studies show that average summertime submicron marine-source organic aerosol concentration over remote oceanic regions can be $\sim 400 \text{ ng m}^{-3}$ (Meskhidze et al., 2011), several orders of magnitude higher than $1\text{--}2 \text{ ng m}^{-3}$ used in previous calculations (Klippel and Warneck, 1980). Experimental studies with concurrent characterization of ambient trace gases, organic aerosol concentration and surface ocean chemical composition, supplemented by aircraft and satellite data may be required to fully explore the complex mechanism of HCHO formation over the Mediterranean and its implications for the air quality in the region.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/11/12787/2011/acp-11-12787-2011-supplement.pdf>.

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